

Polyunsaturated Fatty Acid Retarders in the Emulsion Polymerization of GR-S Synthetic Rubber

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WALDO C. AULT, B. A. BRICE, MARGARET L. SWAIN, B. B. SCHAEFFER,¹ and M. J. COPLEY,²
Eastern Regional Research Laboratory,* Philadelphia 18, Pennsylvania

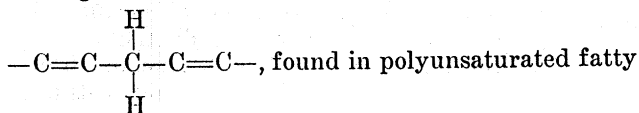
THE importance of scientific research in retaining existing markets for fats and oils, while at the same time extending their uses to new fields, has been well illustrated by the progress made during prosecution of the government's synthetic rubber program. At the beginning of the program tallow soaps were adopted as emulsifiers in the emulsion polymerization process for manufacture of butadiene-styrene synthetic rubber, GR-S. The standard recipe called for 5 parts of soap per 100 parts of monomers, and with the eventual need for at least 800,000 tons of rubber annually, the quantity of suitable soap required would exceed 100 million pounds annually. The early soap specifications included use of relatively high grade tallow, with maximum iodine number of 52, a difference between iodine number and thiocyanogen number not to exceed 6, and a negative test for insoluble bromides.

Two serious difficulties involving emulsifiers arose early in the program. Erratic rates of polymerization were observed with different batches of soap which met the specifications in use then. These variations prevented establishment of a uniform cycle of plant operations. The second difficulty was a critical shortage of high grade tallow. Increasing diversion of edible grade tallow became necessary as production of rubber increased.

To solve these problems the Rubber Reserve Company in 1943 initiated a soap development program for government synthetic rubber. Some of the results of this program were reported before the American Oil Chemists' Society by Burke (7) and have appeared in various publications by Semon (16), Dunbrook (8), and Wilson and Pfau (20). Research at this Laboratory in which various rubber companies, soap manufacturers and universities have collaborated by contributing specialized techniques established the fact that polyunsaturated fatty acid components of the tallow soap emulsifiers acted as retarders in the emulsion polymerization; that variations in the content of polyunsaturated acids undetected by iodine value minus thiocyanogen value (I.V.—T.V.) differences resulted in variable conversion rates; and that selective hydrogenation of the fat stock was a successful remedy for the difficulties encountered.

Although many possible theories were advanced to explain the erratic behavior of the tallow soaps as emulsifiers, the supposition that varying amounts of unidentified "retarders" were present in the soaps seemed most plausible. From a consideration of the composition of tallow, it seemed probable that such retarders if present would be found in one or more of the following groups: a) naturally occurring antioxidants and other congeners, b) polyunsaturated acids present in tallow in small amounts, or, c) metal-

lic impurities in the soap. Substantial basis existed for suspecting these substances of retarding action. For example, synthetic antioxidants exert a great retarding influence. Also diene structures of the type



acids and certain hydrocarbons were very damaging (9a) if present in significant amounts.

To discover whether any of the naturally occurring antioxidants affected the polymerization we obtained authentic samples of lecithin and tocopherols, the antioxidants most likely to be present in tallows. These were supplied to collaborators at several places, including the University of Illinois and the University of Minnesota, who conducted the polymerization experiments necessary to establish whether these substances had any "retarding" effect. Lecithin had no effect in amounts exceeding those likely to occur in tallow. Tocopherols did have a significant retarding effect but only in percentages substantially larger than are likely to occur in an animal fat such as tallow. When the soap contained 0.1% tocopherol, about 5% less polymer was formed in unit time than when the standard soap was used. This difference of 5% was uniform throughout the polymerization. Similar results have been reported by Wilson and Pfau (20) from their experiments, using Eastman Kodak lecithin, but they report slight if any effect from α -tocopherol. This difference may be related to the fact that α -tocopherol has less antioxidant action than other forms of tocopherol (10).

Simultaneously experiments were started in an effort to evaluate the possible effect of the soaps of the various fatty acids likely to occur in tallow. Highly purified saturated and unsaturated fatty acids were prepared at the Eastern Regional Research Laboratory for test in bottle scale polymerization by other collaborators. The acids included:

Stearic Acid: Pure stearic acid was prepared by crystallization from acetone of hydrogenated soybean oil fatty acids obtained through courtesy of Procter and Gamble Company. The acid had the following properties: m.p. 69-70°C., acid no. 198.7, and iodine no. 0.0.

Palmitic Acid: Relatively pure palmitic acid was prepared by crystallization from acetone of a commercial palmitic acid, Neo-Fat 1-51. The acid had the following properties: m.p. 57.3-60°C., acid no. 219, iodine no. 0.25.

Pure Unsaturated Acids

Oleic Acid: Relatively pure oleic acid was prepared from red oil by the process described by Swern, *et al.* (19), which involves low temperature crystallization from acetone and fractional distillation. The acid had an iodine number of 88.2. Although purer oleic acid could possibly have been prepared more readily from

* One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

¹ Present address: Mathieson Alkali Works Inc., Niagara Falls, N. Y.

² Present address: Western Regional Research Laboratory, U. S. Department of Agriculture, Albany, Calif.

olive oil, it seemed desirable to use starting material from animal sources in case isomers assumed to be present might have been a source of the difficulties in polymerization.

Linoleic Acid: Debromination linoleic acid (75 grams) was prepared by bromination of corn oil acids, isolation of the solid bromides, reduction of the resulting crystalline tetrabromostearic acid with zinc in absolute methanol, saponification, and fractional distillation of the free acid. The acid had the following properties: iodine no. 181.9, neut. equiv. 281.3.

Linolenic Acid: Debromination linolenic acid (75 grams) was prepared by bromination of perilla oil acids, isolation of the solid bromides, reduction of the crystalline hexabromostearic acid with zinc in absolute methanol, saponification, and fractional distillation of the free acids. The acid had the following properties: iodine no. 272.8, neut. equiv. 277.3.

α -Eleostearic Acid: Pure α -eleostearic acid, m.p. 49.3°C., was prepared from the fatty acids of authentic tung oil by four fractional crystallizations from petroleum ether.

β -Eleostearic Acid: Pure β -eleostearic acid, m.p. 72°C., was prepared from the fatty acids of tung oil which had been isomerized by sulfur in the presence of light. Two crystallizations from petroleum solvent gave the pure product.

Realizing that the more important polyunsaturated acids might be required for pilot-plant experiments in quantities hardly feasible to prepare in a highly purified state with the time and facilities at our disposal, we also prepared concentrates of linoleic and linolenic acids. Preparation of such concentrates by a method that did not involve the bromides also seemed desirable because of the possibility that isomers in the debromination linoleic (13) and linolenic acids might influence the results obtained during polymerization tests. To lend validity to the results it was desirable to have accurate analyses on both the linoleic and linolenic acid concentrates and to be certain that at least one of them was essentially free of the other. Accordingly a linoleic acid concentrate that contained no more than traces of linolenic acid was prepared from corn oil.

The following concentrates of polyunsaturated acids were prepared:

Linoleic Acid: A concentrate of linoleic acid (6 pounds) was prepared by low temperature crystallization and fractional distillation of corn oil fatty acids. The acid had an iodine number of 166.7 and a thiocyanogen number of 88.0. This analysis corresponds with that of a mixture of 87.0% linoleic acid, 10.3% oleic acid, and 2.7% saturated acids. It contained not more than traces of linolenic acid.

Linolenic Acid: A concentrate of linolenic acid (6 pounds) was prepared by low temperature crystallization and fractional distillation of perilla oil fatty acids. The acid had an iodine number of 237.5 and a thiocyanogen number of 144.5. This analysis corresponds with that of a mixture of 76.0% linolenic acid, 8.9% linoleic acid, and 15.1% oleic acid.

In addition, miscellaneous acids were prepared in different degrees of purity for limited experimentation. The most important of these were:

Dilinoleic Acid: Dilinoleic acid purified by molecular distillation, was furnished through the courtesy of J. C. Cowan of the Northern Regional Research Laboratory.

Phenylstearic Acid: This acid was prepared by the method of Stirton and Peterson (17).

Conjugated Octadecadienoic Acid: A concentrate of this acid containing about 60% conjugated material was prepared by the procedure described by Kass and coworkers (11).

By use of soaps made from these purified fatty acids in bottle scale polymerization tests it was found that stearic, palmitic, and monoethenoic acids, such as the oleic acid from red oil, did not affect the polymerization rate. The retarding effect of polyunsaturated acids however was pronounced. As previously reported (7, 8), over the probable range of occurrence in tallow, that is up to about 10% concentration in the emulsifier, each per cent of linoleic acid caused a corresponding decrease of 1.3% in conversion of monomer to polymer under the standardized conditions of the test. The effect of linolenic acid was even more marked; in the same range each per cent of this acid caused a corresponding decrease of 4.0% in monomer conversion. Conjugated trienoic soaps (α and β eleostearic acids) had a retarding action of 3.3% for each per cent present, only slightly less than that of linolenic acid. Conjugated diene soaps were without appreciable retarding action. These results are in agreement with those reported independently by Wilson and Pfau (20).

Reliable information regarding the fatty acid composition of commercial tallows was not available. Some information of considerable value regarding authentic tallows existed, but commercial tallows are not strictly defined as to source of fat but rather by titer (1). Such information as was available however indicated that in view of the retarding action exerted by polyunsaturated acids, the variations in performance of the soap could be ascribed largely, if not exclusively, to variations in the polyunsaturated fatty acid content of the tallows. Moreover such variations would not be detected by the analytical methods which were being used for the purpose. The specifications which permitted the iodine number and thiocyanogen number to differ by a value up to 6 did not exclude linoleic acid or fix the linoleic acid content at any particular level. Calculation shows that the soaps could fall within this limit while the linoleic acid content ranged from none to a maximum of about 6.6%, provided other polyunsaturated acids were absent. This alone would permit a fluctuation in yield of rubber of about 8.6%.

In a similar manner a negative test for insoluble bromides, although the best test available at the time, by no means guaranteed the absence of linolenic and arachidonic acids. It has been known in a general way for some time that ether-insoluble bromides do not always precipitate even when 2 or 3% of linolenic acid is present. For example, soybean oil fatty acids frequently give a negative hexabromide test (12), despite the fact that soybean oil contains 3 to 8% linolenic acid. An important reason for this failure of the method probably is connected with the solubility effect which the various bromo-derivatives exert on each other. Remembering that each per cent of linolenic acid causes a decrease of 4.0% in monomer conversion, it can readily be seen that the deficiency of this method of analysis would permit variations of serious magnitude.

In view of the foregoing facts it was mandatory that a more reliable and precise method be developed for examination of the fats to be used in emulsifier

soap manufacture. Fortunately the basis for such a method was available in the work of Kraybill and coworkers (2, 15) and others (3, 6, 11) on spectrophotometric methods of analysis for nonconjugated and conjugated polyethenoid components of fats and oils. The former investigators had developed a method of analysis for the nonconjugated components which involved conversion of these components to their conjugated isomers by alkali-isomerization under prescribed conditions followed by ultraviolet absorption measurements. Unfortunately however the work which had been done left something to be desired when attempts were made to apply the existing methods to materials having such small proportions of polyunsaturated constituents found in animal fats and their soaps, partially hydrogenated fats, and purified fatty preparations.

The modified method which was developed (4, 4a, 15a) comprised measurement of the ultraviolet absorption of a sample before and after isomerization, the latter accomplished in an improved medium; correction for extraneous absorption; correction for conjugated constituents originally present and remaining undestroyed by the isomerization treatment; and calculation of the proportions of conjugated and nonconjugated diene, triene, and tetraene fatty acid constituents in the sample. By this method it was possible for the first time to analyze tallows, greases, and soaps for polyunsaturated constituents precisely and in a reproducible manner even when they were present in small proportions. Although more recent work, done largely in this laboratory (18), has indicated that earlier results were somewhat in error chiefly because it was necessary to use absorption coefficients based on debromination acids, these errors were well within the limits of uncertainty of results at the low levels of occurrence of polyunsaturated acids in tallow.

A number of possible methods were considered for removing polyunsaturated constituents from the soaps or rendering them innocuous during the polymerization process. These included isomerization, oxidation, polymerization, and selective hydrogenation. Because of economic and plant considerations and also in view of experimental data not presented here, selective hydrogenation of the fat was selected as the remedy. The spectrophotometric method of analysis was used as the control and furnished the chief means for drawing the specifications in order to obtain the results needed.

Nearly complete hydrogenation of the fats to be used in soapmaking offered several disadvantages. One was the large consumption of hydrogen, with the resulting expense. Another was that the resulting soaps consisting almost completely of soaps of C_{16} and C_{18} saturated acids would be difficult to handle and more insoluble than soaps made from fats containing a substantial amount of monoethenoic acids. Consequently it was desirable to hydrogenate as selectively as possible only to the point where the polyunsaturated acids were substantially eliminated while the monoethenoic content was reduced to the least possible extent. This has proved to be possible. Table I shows results obtained in experiments using a wide variety of fats. In addition to analytical data on the tallows and fatty acids this table gives polymerization indices (P.I.), "predicted" relative conversions to polymer, and "corrected" relative conversions to polymer for soaps made from a

variety of crude fats and refined bleached fats as well as from fats hydrogenated to different degrees.

The polymerization index was calculated from the spectrophotometric analysis as follows: Polymerization index (P.I.) = % linoleic + 3 (% linolenic + % arachidonic). This is based on the finding that the retarding action of linolenic acid is approximately three times that of linoleic acid.

The actual depressing action of arachidonic acid upon the polymerization reaction was not determined, but it was assumed to be at least as active as linolenic acid. Since the percentage of arachidonic acid in hydrogenated soaps was usually nil, no serious errors could result from this assumption. In the final revised specifications an upper limit of 0.9 was set for the P.I. (21).

The "predicted" relative conversion was calculated in each case from the polymerization index by use of the equation:

$$\text{"Predicted" Relative Conversion} = 100 - (1.3 \times \text{P.I.}).$$

The quantity in parentheses is the calculated drop in conversion due to the presence of the polyunsaturated retarders.

In calculating the "corrected" relative conversions from observed conversions, corrections were made for the polyunsaturated content of the "standard" silicate free soap flakes used as controls. The formula used was:

$$\text{"Corrected" observed Relative Conversion} = \frac{100 \times \text{Relative Conversion}}{\text{"Predicted" Conversion of Standard Soap}}$$

Correction of relative conversion values to the same basis implies that all other variables are constant, which is not true. Nonetheless the corrected data are undoubtedly at least as reliable as the uncorrected data and are more concise for presentation. Results obtained by thiocyanometric as well as by spectrophotometric methods of analyses are shown in nearly all cases. More complete spectrophotometric data for many of these samples have been reported previously (4a).

The results obtained by bottle scale polymerization tests were confirmed in pilot plant and plant scale operation with the result that soap made from a selectively hydrogenated fat that meets the specifications has been used in all the GR-S plants operated under the supervision of the Rubber Reserve Company.

Two rather important difficulties have been reported in the use of selectively hydrogenated tallow soap. The first is the lack of tack in the GR-S made with the soap; the second is a rather wide variation in the amount of modifier required to keep the polymerization rate constant. A "disproportionated rosin soap" has been used to impart increased tack (8) while evidence indicates (5) that certain metallic contaminants of the soap, particularly nickel or nickel soaps, may be responsible for variations in the amount of modifier required. Although this has been controlled empirically by bleaching and refining before hydrogenation (9), the real nature of the difficulty has not yet been pointed out conclusively.

The chief accomplishments of this research were a) proof that linoleic and linolenic acids in soaps used as emulsifiers in synthetic rubber manufacture were a cause of irregularities in the polymerization reaction and b) the development of a spectroscopic

TABLE I
Analytical and Bottle Scale Polymerization Data

Sample No.	Description	Tallow		Fatty Acids			Polymerization Index	"Predicted" Relative Conversion	Soaps	
		Thiocyanometric Analysis		Spectrophotometric Analysis					"Corrected" Observed Relative Conversions	
		I. V.	I. V.-T. V.	Linoleic	Linolenic	Arachidonic			Univ. of Illinois	Univ. of Minnesota
1C	Crude fats	54.4	7.6	5.1	0.13	0.15	5.9	92	88	
2C		49.8	4.8	3.9	0.15	0.17	4.9	94	89	
3C		50.3	5.7	3.7	0.19	0.09	4.5	95	95	
4C		57.5	7.5	6.7	0.12	0.20	7.7	90	88	
5C		57.8	7.8	6.7	0.18	0.17	7.8	90	87	
1A		47.6	5.2	3.8	0.29	0.14	5.1	93	90	
2A		50.0	7.4	4.3	0.45	0.35	6.7	91	87	
3A		52.3	7.4	4.7	0.11	0.29	5.9	92	84	
4A		52.8	8.0	4.5	0.53	0.30	7.0	91	83	
5A		60.4	10.3	8.1	0.33	0.26	9.9	87	81	
1RB	Refined bleached fats	51.8	5.8	5.0	0.17	0.13	5.9	92	89	
2RB		50.2	4.3	4.0	0.22	0.10	5.0	93	93	95
3RB		50.0	4.5	3.7	0.22	0.09	4.9	94	94	
4RB		56.8	8.3	6.7	0.17	0.17	7.0	91	87	
5RB		57.3	8.0	6.6	0.23	0.13	7.7	90	87	89
1B				4.4	0.27	0.21	5.8	92	88	89
2B				6.0	0.20	0.20	7.2	91	87	86
3B				3.7	0.24	0.11	4.8	94	91	95
4B				4.5	0.32	0.24	6.2	92	89	90
5B				8.1	0.31	0.20	9.6	87	82	84
2AH1	Fats 2A and 5A hydrogenated to different levels	40.0	1.4	0.26	0.02	0.00	0.3	100	102	103
2AH2		26.9	1.0	0.10	0.01	0.00	0.1	100	100	103
5AH1		47.8	0.8	0.35	0.02	0.00	0.4	99	103	106
5AH2		36.5	0.3	0.11	0.02	0.00	0.2	100	103	104
5AH3		22.8	0.6	0.11	0.05	0.00	0.2	100	102	103
2RBH1	Fats 2RB and 5RB hydrogenated to different levels	41.1	2.7	0.11	0.04	0.00	0.2	100	99	
2RBH2		32.6	1.7	0.12	0.02	0.00	0.2	100	106	
2RBH3		20.8	1.6	0.12	0.02	0.00	0.2	100	101	
5RBH1		39.7	2.5	0.14	0.02	0.00	0.2	100	105	103
5RBH2		31.0	1.6	0.09	0.03	0.00	0.2	100	105	104
5RBH3		22.2	1.5	0.11	0.04	0.00	0.2	100	103	
	Silicate-free soap flakes			1.9	0.16	0.04	2.5	97 (12 hrs at 50°C.)	100	

method of analysis suitable for even small amounts of polyunsaturated acids, permitting the drafting of new and improved specifications (21). Development of improved emulsifiers has contributed to the introduction of a continuous process for polymerization of GR-S (7, 9). Moreover the spectroscopic method of analysis is proving to be a valuable tool in connection with other research on both industrial and food uses of fats. Its adoption as an official method of the Society is receiving serious consideration.

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